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**Atmospheric Contamination  
in USS TECUMSEH**

[Unclassified Title]

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## CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
DETAILS OF THE TECUMSEH INCIDENT	2
Medical Observations	2
Operation of Atmosphere Control Equipment	2
Miscellaneous Observations	3
Corrective Action During Patrol	4
ANALYSIS OF SAMPLES FROM USS TECUMSEH	4
Lithium Carbonate Sample	4
Compressed Nitrogen Sample	5
Sample of Compressed Air from High-Pressure Bank	5
Main Filter Carbon Samples	7
CORRELATIVE EXPERIMENTAL WORK	9
Significance of Positive Reading on Draeger Trichloroethylene Detector Tube	9
Preparation and Physical Properties of Dichloroacetylene	12
The Possible Role of Atmosphere Control Equipment and Other Machinery in the Synthesis of Harmful Chemicals	12
WHAT TOXIC AGENT CAUSED THE TECUMSEH ILLNESSES DURING FIRST PATROL?	13
Dichloroacetylene	14
Vinylidene Chloride	16
Methyl Chloroform	16
Trichloroethylene	16
Tetrachloroethylene	17
Freon-Type Compounds	17
Various Chlorinated Hydrocarbons	18
Lithium Carbonate Dust	18
Phosphine	18
Other Candidate Toxic Agents	19
CONSEQUENCES OF THE TECUMSEH INCIDENT	19
CONCLUSIONS	20
RECOMMENDATIONS	20
ACKNOWLEDGMENTS	21
REFERENCES	22

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ABSTRACT  
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A high percentage of the personnel of USS TECUMSEH (Blue) became ill after about 30 days' submergence during the ship's first patrol. In many cases symptoms were quite severe. The characteristics of the illnesses strongly implicated a toxic agent rather than infection as the cause. Study of atmosphere samples and related information indicated that the illness was related to the high content of chlorinated hydrocarbons in the atmosphere. Although the specific toxicant has not been identified, two of the most likely suspects are dichloroacetylene and vinylidene chloride. There is also the possibility of the combined effect of a number of halogenated compounds. Elimination of chlorinated compounds in nuclear submarines should be an immediate goal.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problems C08-18, C08-30,  
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ATMOSPHERIC CONTAMINATION IN USS TECUMSEH  
[Unclassified Title]

INTRODUCTION

A potentially serious threat to the continuing and successful operation of the United States FBM submarine fleet occurred early in 1965 (1,2). The Blue Crew of USS TECUMSEH (SSB(N) 628) had been submerged for about 30 days during its first patrol when a high percentage of the personnel on board became ill. The symptoms first appeared as a feeling of lassitude or drowsiness, followed by nausea and vomiting; and within 48 to 72 hours the illness had spread throughout the crew, with many becoming so ill that 26 men were removed from watch duty. In some cases, vomiting was so severe that intravenous feeding was required.

The nature of the illness strongly implicated an unknown atmospheric contaminant as the causative agent (3). The ship's force took prompt action in an attempt to localize and identify the source of the contaminant and eliminate it. Certain suspected items were jettisoned. The commanding officer of TECUMSEH finally had to resort to snorkel ventilation, which may well have averted dangerous, perhaps tragic, consequences. Samples of the atmosphere were taken and together with associated suspected materials were sent to NRL for analysis (4,5). Laboratory work was begun immediately upon receipt of these samples because of the very serious implications of this incident. There was no reason to assume that this grave situation could not be repeated on this submarine or that it would not occur in other submarines of the fleet. It was, therefore, imperative to determine the cause of the illnesses and take necessary action in an effort to prevent any further occurrences in TECUMSEH or any other nuclear submarine.

Analyses of the samples from TECUMSEH were given the highest priority at this Laboratory. All available information was gathered and studied relating to symptoms, operation of atmosphere control equipment, and possible sources of atmospheric contamination (1,2,4,6). Consultations with personnel of the Bureau of Ships, the Bureau of Medicine and Surgery, and particularly with Capt J. Siegel of the U.S. Navy Toxicology Unit, Bethesda, Maryland, were frequent and detailed. Mr. R. O. Bullock of the Bureau of Ships and Dr. J. E. Johnson of NRL interviewed many personnel at Submarine Base, Pearl Harbor, including a substantial number from the Blue Crew of TECUMSEH. Cdr B. K. Hastings, Force Medical Officer, ComSubPac, arranged the many conferences, including radiotelephone conversations with SubRon Fifteen and the Gold Crew of TECUMSEH.

Detailed recommendations were made (7) for operation of atmosphere control equipment, etc., before the Gold Crew of TECUMSEH set out on patrol. The second and third patrols of TECUMSEH were accomplished with no recurrence of the problem. Personnel remained well and morale high. These improved conditions probably resulted to some extent from strict adherence to the recommended operating procedures.

The analyses of the samples from the first patrol of TECUMSEH were the most detailed ever made for an FBM submarine and are related extensively in this report because of the importance of the data and the subsequent conclusions. Laboratory studies on other aspects of the problem were carried out and are reported also.

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## DETAILS OF THE TECUMSEH INCIDENT

It is desirable to present a complete brief of the pertinent events which occurred aboard TECUMSEH. The facts were collected from written reports of TECUMSEH (1-6) and from oral conferences with personnel of the Blue Crew of TECUMSEH.

### Medical Observations

The medical history of this occurrence is summarized in the following quotation (1): "The nausea and vomiting which resulted in the removal of cases eight through thirty-four from the watch bill was only one of a set of symptoms experienced by a majority of the crew during the same period. This set of symptoms, or syndrome, began in the latter part of the ninth week and continued into the middle of the tenth week. The syndrome consisted of a feeling of lassitude or somnolence, nausea, vomiting, aching of the muscles (particularly the muscles of the chest) and constipation. At least 95% of the crew had at least one of the symptoms of this syndrome, the most common being a mild but significant sense of lassitude or a drowsy feeling. Vomiting was experienced on at least one occasion by 75% of the crew. The muscle soreness and constipation appeared during the latter days of syndrome in men who were otherwise well or at least on the road to recovery. Fever and diarrhea were not recorded, and physical examinations were negative. There were no irritant or respiratory symptoms. The most likely etiological agent was thought to be an unidentified atmospheric contaminant as the syndrome appeared to be toxic rather than infectious in nature."

After two nights of ventilation, the crew started to recover, and all personnel were back to near normal by the end of the patrol. The muscle soreness in the chest area persisted in some men for several additional weeks and was apparently not due entirely to vomiting. In thinking back later, some men recalled having tightness of breath as early as a few days before the serious symptoms began. Although the general symptoms were widespread throughout the crew, there was general agreement that those with stations aft were somewhat more ill. There seemed to be no discrimination between smokers and nonsmokers; both groups developed symptoms of approximately equal severity.

### Operation of Atmosphere Control Equipment

**CO/H<sub>2</sub> Burners** — Because the pressure drop across the catalyst bed had risen to an abnormally high level during transit, the Hopcalite was removed during refit, stirred up, and replaced in the bed. The bed was topped off with fresh catalyst and the differential pressure returned to normal.

The No. 1 CO/H<sub>2</sub> burner experienced a series of heater failures during the first two weeks of patrol. On Jan. 31, 1965, a heater lug burned off; three heater elements were replaced. On Feb. 9, 1965, the burner again failed to maintain proper operating temperature. Examination showed that heater terminals were burned off. Heater elements, terminals, leads, and relay were replaced. On Feb. 11, 1965, No. 1 burner failed again, requiring replacement of three more heater elements. It should also be noted that No. 1 burner had failed for similar reasons on at least two occasions prior to first patrol. Why this repeated failure of the heaters was limited to Burner No. 1 and its basic cause are not clear.

During Patrol One, the burners were operated in several different ways to investigate the effect on corrosion which was occurring in Auxiliary Machinery Room 2 (AMR-2).

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During the first ten days of patrol, the burners were operated with the lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) filters removed. No appreciable change in the corrosion rate was noted during this period, but the amount of white dust deposited on surfaces in AMR-2 seemed to be somewhat less than during previous operation with the  $\text{Li}_2\text{CO}_3$  filters in place. The dust during this period seemed to have a grayish appearance and could have contained powdered Hopcalite from the burner discharge. When the  $\text{Li}_2\text{CO}_3$  filters were reinstalled, white dust again appeared in AMR-2, with no apparent change in corrosion rate. The dust was found to be quite alkaline, and it was assumed that it was  $\text{Li}_2\text{CO}_3$  being blown out of the filters. The greatest deposit of white dust occurred in AMR-2. Some dust migrated as far as the fan room. It was not noticeable in operations or forward rooms.

The  $\text{Li}_2\text{CO}_3$  was prepared from anhydrous  $\text{LiOH}$  in the emergency  $\text{CO}_2$  scrubber. At the end of the patrol, 22 lb of  $\text{Li}_2\text{CO}_3$  was needed to refill the burner filters, but some of this loss was probably due to settling.

Main Filter Carbon — The main carbon bed was charged with fresh carbon at the beginning of the patrol. A fresh charge was inserted at the 20th day and again on the 34th day of patrol (fourth day of toxic symptoms).

Mark II Mare Island  $\text{CO}_2$  Scrubbers — The difficulties with the MEA scrubbers were not noticeably more severe than usual. It was felt by ship's personnel that the scrubbers probably did not contribute to the illnesses.

Electrostatic Precipitators — On a number of occasions, one or more of the ESP units required extra maintenance and cleaning to correct arcing. For example, the galley precipitator vibrated excessively, causing arcing, unless the ventilation rate was kept at low speed. Other fans were operated at low speed for similar reasons. The Trion precipitators on the sump vents appeared to give satisfactory performance. The other precipitator troubles were extensive enough that the ship, after patrol, requested design improvements to increase the reliability and ease of maintenance of electrostatic precipitators.

Atmosphere Analyzer, Mark IV — The Mark IV Atmosphere Analyzer gave very little trouble except for difficulties with the Freon-11 (F-11) channel. It was within calibration at all times, and the levels of all atmosphere components fell within normal limits. For example,  $\text{CO}_2$  ranged from 1.0 to 1.5%, CO less than 25 ppm, and F-12 between 100 and 130 ppm. The F-11 channel was inoperative during the period of illnesses, having developed a faulty detector. The spare detector was also defective. The F-11 readings before breakdown were 5 to 15 ppm. Daily leak checks of the F-11 plants were negative.

Refrigeration Plants — One F-11 plant stopped operating some days before the symptoms began. Fifty pounds of F-11 was required to refill the unit. It was stated that such a leak would not necessarily have gone into the ship's atmosphere because of the purge system, but might have been pumped overboard.

#### Miscellaneous Observations

Certain other details which are pertinent to the problem are noted as follows:

1. In an atmosphere survey made after the appearance of medical symptoms, using all the standard Draeger tubes, no positive indication was obtained except for the trichloroethylene tube which read 25 ppm. No trichloroethylene was known by ship's personnel to be on board. (Subsequent analysis of a sample of carbon from the main filter showed that a relatively high content of trichloroethylene had been present on board.)



2. An acetylene bottle in the submarine welding and cutting set located in the engine room was found to be leaking very slowly. It was believed to have lost 16 cu ft (STP) during a period of unknown duration. The acetylene bottle was jettisoned after gaging the pressure.

3. A few days before the onset of medical symptoms, a sweet, unpleasant, sour odor was noted by ship's personnel in the vicinity of the lithium bromide plant. It was obnoxious and unusual and was not identified.

4. Dr. Robinson (the ship's medical officer) and others noticed that the recoil air from blowing the sanitary tank was particularly foul-smelling the day before the first illness. Engine room personnel reported that the drinking water tasted bad, but this taste was not verified by a hospital corpsman who checked it. Many reported that cigarettes tasted bad and they could not stand the coffee. These may well have been early symptoms in prelude to the nausea which developed later.

#### Corrective Action During Patrol

A number of measures were taken aboard TECUMSEH when the severity of the symptoms became apparent, both in an effort to treat the personnel and to remove the source of the toxic contamination.

1. The most drastic step was snorkel ventilation for a period of 2 to 6 hours each night for five consecutive nights, beginning the third night after the symptoms began.
2. The service air bank was discharged overboard and recharged during a period of snorkel ventilation.
3. The main filter bed was recharged with fresh carbon, although it had been changed about two weeks earlier.
4. The  $\text{Li}_2\text{CO}_3$  filter was removed from the  $\text{CO}/\text{H}_2$  burner exhaust.
5. Potable water was chlorinated.
6. Suspected foods were jettisoned.
7. The leaking acetylene cylinder was jettisoned.

#### ANALYSIS OF SAMPLES FROM USS TECUMSEH

A description of each sample (taken from Refs. 4 and 5) follows, along with a summary of the analytical data obtained at NRL pertinent to the sample. Only a brief description of analytical equipment and procedures is given here in the interest of brevity.

##### Lithium Carbonate Sample

The sample of  $\text{Li}_2\text{CO}_3$  from the  $\text{CO}/\text{H}_2$  burner filter bed weighed 13 lb. Analysis for chloride showed 1.4% as hydrochloric acid (HCl). Calculated on a basis of 90 lb total bed weight and 30 days' exposure, the HCl which was absorbed is estimated at about 1.0 ppm in the burner effluent. There is no way to estimate the amount of HCl which was

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intercepted by corrosion of the cooling coils or which proceeded beyond the  $\text{Li}_2\text{CO}_3$  scrubber.

#### Compressed Nitrogen Sample

The compressed nitrogen sample from TECUMSEH, contained in a compressed gas cylinder, was stated to be nitrogen from the supply used for purging the oxygen generators. By use of gas chromatography and infrared spectroscopy, it was established that this sample was indeed essentially 100% nitrogen, with a trace of oxygen. No organic compounds or other inorganic contaminants were detectable.

#### Sample of Compressed Air from High-Pressure Bank

The compressed air sample received at NRL had been taken aboard TECUMSEH after development of symptoms, but before outboard ventilation, by bleeding down one of the 4500-lb banks, then pumping ship's air into it via the high-pressure air compressor. This compressed air sample was analyzed by infrared spectroscopy to identify the principal low-molecular-weight components. The results are listed in Table 1. Methane and F-12 were determined also by the NRL Total Hydrocarbon Analyzer, as noted. The first three components, methane, F-12, and carbon monoxide, were present in concentrations fairly normal to nuclear submarine atmospheres. The significance of the acetylene concentration found is discussed in a later portion of this report. The presence of carbon tetrachloride ( $\text{CCl}_4$ ) shown by infrared spectroscopy was confirmed by gas chromatography, but the indication by this method is that the sample contained less than 0.5 ppm. The presence of as much as 0.5 ppm of  $\text{CCl}_4$  should be of some concern but may not be of significance toxicologically.

Table 1  
Low-Molecular-Weight Contaminants  
in TECUMSEH Air Bank Sample

Compound	Concentration (ppm)	
	IR Analysis	THA*
Methane ( $\text{CH}_4$ )	48 ± 5	50
F-12	43 ± 5	52
Carbon monoxide (CO)	17.5 ± 5	-
Acetylene ( $\text{C}_2\text{H}_2$ )	5 ± 2	-
Carbon tetrachloride ( $\text{CCl}_4$ )	0.3 to 1.0	-

\*Analysis by the NRL Total Hydrocarbon Analyzer (8).

The air sample, as was expected, contained a large number of compounds which may be labeled as trace organic contaminants. The total concentration of these compounds, as determined by the NRL Total Hydrocarbon Analyzer, was 30 micrograms per liter, which is not unusually high. However, it was of particular interest to identify and

determine the amounts of the volatile chlorinated hydrocarbons in the air sample, since the medical symptoms appeared to indicate that chlorinated compounds might be involved.

These detailed analyses were made by separating the compounds in a gas chromatograph. The halogenated compounds listed in Table 2 were identified by trapping the pertinent gas chromatographic peaks and subjecting them to mass spectrometry. The quantitative estimates given in Table 2 were made by gas chromatographic techniques. Vinylidene chloride and dichloroacetylene were found under the same peak, and the relative concentration of the latter was estimated by mass spectrometry. It was shown that dichloroacetylene was not produced from vinylidene chloride in either the gas chromatograph or mass spectrometer.

Table 2  
Gas Chromatographic-Mass Spectrometric Analysis of  
Halogen Compounds in TECUMSEH Air Bank Sample

Compound	Formula	Concentration (ppm)
F-12	$\text{CCl}_2\text{F}_2$	52
F-114	$\text{CClF}_2 - \text{CClF}_2$	1.5
F-11	$\text{CCl}_3\text{F}$	4.0
F-113	$\text{CCl}_2\text{F} - \text{CClF}_2$	0.6
Vinylidene chloride	$\text{CH}_2=\text{CCl}_2$	2.0
Dichloroacetylene	$\text{ClC}\equiv\text{CCl}$	0.15
F-114B2	$\text{CBrF}_2 - \text{CBrF}_2$	Trace
Methyl chloroform	$\text{CH}_3\text{CCl}_3$	1.0

How representative the concentrations of the contaminants in the air bank sample are of those present in the ship at the time of the illness cannot be determined accurately. The bank was charged at the time of the trouble and mixed with an unknown amount of air already there. The ship's engineer estimated that only 20 to 50% of this sample may actually have been air from the ship at that time. Also the effect of the charging process on the contaminant cannot be assessed. This air is dried, filtered, and passed through an alumina bed in the compressor system.

Based on the F-12 concentration (100 to 130 ppm) reported by the Atmosphere Analyzer aboard ship, and the 50 ppm of F-12 found in the air sample, it is possible that the levels of chlorinated compounds in the atmosphere were at least 2 to 3 times those found in the air bank sample. Preferential removal of the higher boiling chlorinated hydrocarbons may have occurred in the air compressor system.

### Main Filter Carbon Samples

Three carbon samples which were received at NRL were identified as follows:

NRL-C-389, sample taken from main filter after the fourth day of toxic symptoms (34th day of patrol), exposure about 12 days. The exposure time of this carbon covered the period of developing symptoms and should therefore be of exceptional importance.

NRL-C-390, sample taken at end of patrol, exposure estimated to be 6 to 8 days. This included the periods of snorkel ventilation.

NRL-C-391, control (unused) sample.

The analytical data on these carbon samples is contained in Table 3. Discussion of them follows:

Table 3  
Steam Desorption of Main Filter Carbon from TECUMSEH

Sample No.	Exposure (days)	Total Weight Loss (%)	Desorbed Oil*	
			Total Weight (%)	Heavy Oil Weight (%)
C-389	12	21.9	6.7	1.4
C-390	6-8†	23.1	0.5	0.0
C-391	0	13.0	0.0	0.0

\*Percentages are based on the weight of residual carbon after steam desorption of the samples. The condensate collected in the trap consisted of three phases: a light oil phase above the water, water phase, and a heavy (denser) oil below the water.

†Includes periods of snorkel ventilation.

C-391. No organic phase was found by steam desorption in the Laboratory (9). This indicates that the unused carbon aboard was clean and did not itself introduce atmospheric contamination.

C-390. As shown in Table 3, this carbon yielded 0.5% of an oil which was lighter than water. Examination of this oil by gas chromatography showed it to be very similar to the light oil from C-389.

C-389. In addition to steam desorption, some of this carbon was desorbed by a vacuum technique. Major components of interest which were identified from the vacuum desorbate were F-12, F-11, vinylidene chloride, and methyl chloroform.

Most of the further examination of the C-389 carbon sample was based on oils obtained by steam desorption. As shown in Table 3, the total oil desorbed by steam was 6.7% by weight based on residual carbon. The condensate which was collected in the trap consisted of three phases: a light oil phase (C-389L) above the water, the water, and a

heavy oil (C-389H) below the water. The heavy (denser) oil represented 30% by weight of the water-insoluble desorbate.

**Analysis of Lighter-than-Water Phase, C-389L**— This fraction was examined by the fluorescent indicator adsorption (FIA) method (10) for hydrocarbon types, and the results are given in Table 4. The aromatic hydrocarbon content, 38% by volume, is unusually high. The aromatics in recent submarine oils from carbon have been in the range of 25 to 30% (10).

Table 4  
Hydrocarbon Type Analysis of Light Oil  
C-389L by FIA Method

Fraction	Volume Percent
Aromatics	38
Middle cut*	6
Saturates	56

\*Usually contains olefinic hydrocarbons and other unsaturated compounds.

The aromatics portion is also relatively very volatile, consisting largely of toluene and the xylenes, with more than 90% boiling below n-butylbenzene (bp 183.3°C). Previous samples from other submarines have ranged from 30 to 80% boiling below n-butylbenzene. The boiling ranges of oil C-389 and oil C-390 are very similar, as displayed by gas chromatography, and lower than usually found.

The middle cut in Table 4 is even more volatile than the aromatics fraction or the whole oil, C-389L. The two largest peaks obtained by gas chromatography of the middle cut were trapped out and analyzed by infrared and mass spectrometry. The largest peak (more than 40% of this fraction) was tetrachloroethylene (bp 122°C). The next largest peak (ca. 20%) consisted of saturated hydrocarbons. Most of the remaining peaks represented very low-boiling compounds.

The lighter-than-water phase, C-389L, contained 8.6% chlorine by weight on elemental analysis (Table 5).

Table 5  
Elemental Chlorine in C-389 Oil

Fraction	Chlorine (Wt-%)
C-389L, light fraction	8.6
C-389H, dense fraction	62.3
Combined oil, calculated	19.6

**Analysis of Heavier-than-Water Phase, C-389H**— The elemental analysis of this fraction, 62.3% chlorine (Table 5), shows that it consisted essentially entirely of chlorine compounds. This fraction was separated into individual components by gas chromatography, using both thermal conductivity and hydrogen flame ionization detectors. Halogenated compounds produce less response than hydrocarbons in the flame detector, whereas thermal conductivity is roughly the same. Comparison of the relative peak heights produced by the two detectors makes it possible to pick out the peaks that could be due to halogenated compounds. The peaks whose relative heights were diminished in the hydrogen flame detector were trapped and analyzed by mass spectrometry. Halogenated compounds which were identified are listed in Table 6. By gas chromatography,

more than 90% of this fraction was shown to be volatile halogenated compounds. No absolute quantitative numbers could be assigned to the individual compounds, but relative values based on thermal conductivity data are indicated in Table 6. Methyl chloroform was the predominant halogenated compound, followed by vinylidene chloride. The relatively large amounts of trichloroethylene, tetrachloroethylene, and F-113 are of special interest also.

Table 6  
Halogenated Compounds Identified in the Heavier-than-Water  
Desorbate (C-389H) from the Main Carbon Bed

Compound	Formula	BP (°C)	Estimated Quantity*
F-11	$\text{CCl}_3\text{F}$	24	+
F-113	$\text{CCl}_2\text{F}-\text{CClF}_2$	48	+++
F-114B2	$\text{CBrF}_2-\text{CBrF}_2$	48	trace
Vinylidene chloride	$\text{CH}_2=\text{CCl}_2$	37	++++
Chloroform	$\text{CHCl}_3$	61	++
1,1-Dichloro-2,2,2-tri-fluoroethane	$\text{CHCl}_2\text{CF}_3$	-	trace
1-Chloro-2,2-difluoro-ethane	$\text{CH}_2\text{ClCHF}_2$	36	trace
Methyl chloroform	$\text{CH}_3\text{CCl}_3$	74	+++++
Carbon tetrachloride	$\text{CCl}_4$	77	+
Trichloroethylene	$\text{CHCl}=\text{CCl}_2$	87	+++
Tetrachloroethylene	$\text{CCl}_2=\text{CCl}_2$	121	+++

\*Relative amounts ranged from +++++ (high) to + (low) to trace (very small).

#### CORRELATIVE EXPERIMENTAL WORK

##### Significance of Positive Reading on Draeger Trichloroethylene Detector Tube

In connection with this submarine atmosphere problem, it was reported that all the available colorimetric gas detector tests were carried out. These were all negative except that an indication of 25 ppm was obtained on the trichloroethylene tube. It is of particular interest to investigate, so far as practicable, the meaning of this indication.

It is not clear whether the gas detector tube used was the older 0.1 trichloroethylene tube or its recently introduced replacement, the 10/a trichloroethylene tube. Both were investigated, with emphasis on the newer 10/a tube, since it probably was the tube used. Details of this work are expected to be published separately (11).

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Although both tubes are quite specific to halide, the halogen does not necessarily have to be present as hydrocarbon halide, since free halogen and some volatile inorganic halides also react. Further, the hydrocarbon halides are not indicated proportionally to their halide content. The manufacturer states that interfering materials which give a positive indication with the 10/a tube are: chlorine (x10), nitrogen dioxide (x2), sulfur dioxide (x1), and hydrochloric acid (x1/3). The number in parenthesis is the indication in ppm for each ppm present in the sample. Materials which have no effect on the indication are: hydrogen sulfide, ammonia, and methyl and ethyl alcohol. Paint thinners do not produce an indication but can appreciably reduce the indication from hydrocarbon halides, apparently by reaction with the free halide formed by the oxidation before the halide can react with the indicator material. This effect can be large and variable depending on the composition of the mixture making up the thinner. It is assumed that the older 0.1 tube has comparable interferences from these materials.

The manufacturer of these tubes has supplied information on the indication which should be obtained with about 15 short-chain aliphatic hydrocarbon halides which are of the type of probable interest here. In addition, a number of tests were made at NRL to confirm the manufacturer's information and to extend the study to other halogenated compounds. In general, the manufacturer's claims were substantially confirmed in all respects. A summary of the combined data is given in Table 1.

It was established that the detector tube indication is additive when several halogenated hydrocarbons are in the same sample. Saturated aliphatic hydrocarbons did not interfere, but unsaturated aliphatic hydrocarbons (olefins) drastically reduced the indication. Analyses of hydrocarbons from nuclear submarine atmospheres in the past have shown that olefin content is very low (10). The analysis of hydrocarbons from TECUMSEH also indicated very little olefin (see Table 4).

It can be concluded from the above information that the 25 ppm indication obtained on the trichloroethylene tube had the following meanings:

1. The indication was not the direct result of refrigerants or methyl chloroform (1,1,1-trichloroethane) in the sampled atmosphere because these compounds give little or no indication with the detector tube. Neither was the indication due to any appreciable extent to the presence of chlorine, nitrogen dioxide, sulfur dioxide, or HCl since these gases should have given indications on other gas detector tubes used or should have caused respiratory irritation.

2. Although the indication of this tube will not identify the particular hydrocarbon halides present in the sample, it is concluded that there was a total concentration of about 25 ppm by volume of reactive hydrocarbon halides in the sampled atmosphere. In the absence of any other knowledge of the halogen compounds, it would be logical to assume that the material producing this indication was a mixture, mainly composed of one or more of the following because of their common use as solvents or because they are decomposition products of common solvents:

1,1,2,2-Tetrachloroethane ( $\text{CHCl}_2\text{--CHCl}_2$ )  
Vinylidene chloride ( $\text{CH}_2=\text{CCl}_2$ )  
1,2-Dichloroethylene ( $\text{CHCl}=\text{CHCl}$ )  
Trichloroethylene ( $\text{CHCl}=\text{CCl}_2$ )  
Tetrachloroethylene ( $\text{CCl}_2=\text{CCl}_2$ )  
Dichloroacetylene ( $\text{CCl}=\text{CCl}$ ).

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Table 7  
Response to Draeger Trichloroethylene Detector Tube

Material	Relative Sensitivity*
$\text{Cl}_2$	10
$\text{HCl}$	trace
$\text{CH}_3\text{Cl}$	0
$\text{CH}_2\text{Cl}_2$	0.1
$\text{CHCl}_3$	0.5
$\text{CCl}_4$	0
$\text{CH}_2\text{ClBr}$	0.2
$\text{CHBr}_3$	1.2
$\text{CCl}_3\text{F}$	0
$\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$	0.2
$\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$	2.0
$\text{CHCl}_2-\text{CHCl}_2$	0.7
$\text{CH}_2\text{Cl}-\text{CHCl}_2$	0.4
$\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$	trace
$\text{CH}_3\text{CCl}_3$	0
$\text{CH}_2=\text{CCl}_2$	1
$\text{CHCl}=\text{CHCl}$	1
$\text{CHCl}=\text{CCl}_2$	1
$\text{CCl}_2=\text{CCl}_2$	1
$\text{CCl}\equiv\text{CCl}$	1.0
$\text{CH}_3-\text{CHCl}-\text{CH}_2\text{Cl}$	1
$\text{CH}_2\text{OH}-\text{CHCl}-\text{CH}_2\text{Cl}$	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$	0

\*Relative to  $\text{CHCl}=\text{CCl}_2$  taken as 1.0.



The analyses of carbon and air samples from USS TECUMSEH actually showed the presence of four of these compounds, vinylidene chloride, trichloroethylene, tetrachloroethylene, and dichloroacetylene, the first three in substantial amounts.

Monochloroacetylene ( $\text{CH}\equiv\text{CCl}$ ) was not available for test but would be expected to produce an indication about equal to its concentration. It might, therefore, be added to the list above.

It was reported by Dr. R. Robinson, USS TECUMSEH (Blue), that a lesser reading was found with the trichloroethylene tube by the Gold crew on Patrol Two, and that the readings on Patrol Three were zero.

#### Preparation and Physical Properties of Dichloroacetylene

The presence of dichloroacetylene,  $\text{CCl}\equiv\text{CCl}$ , in the TECUMSEH air sample was somewhat unexpected, since this compound has been reported to be spontaneously flammable in air (12). However, dichloroacetylene was previously detected, along with monochloroacetylene,  $\text{HC}\equiv\text{CCl}$ , in the desorbate from a carbon sample which had been exposed in a simulated space chamber in which the occupants became ill (13).

A sample of dichloroacetylene was prepared in the laboratory following its discovery in the TECUMSEH air sample. Several hundred parts per million of trichloroethylene in nitrogen were passed over dehydrated KOH at 100 to 130°C and a 50 to 70% yield of dichloroacetylene was obtained. The latter compound by infrared spectroscopy was found to react spontaneously with air at room temperature, forming  $\text{CO}$ ,  $\text{CO}_2$ , and phosgene ( $\text{COCl}_2$ ). Other experiments indicate that dichloroacetylene is stable in air at a level of a few parts per million. There has not been sufficient work done to establish an upper limit for the concentration of dichloroacetylene in air, however. Certain previous work indicates a higher stability in the presence of vapors of some other compounds (19). Further work on the preparation and properties of the chlorinated acetylenes is being carried out.

#### The Possible Role of Atmosphere Control Equipment and Other Machinery in the Synthesis of Harmful Chemicals

Laboratory work is underway on the role of the various atmosphere control equipment and other machinery in the possible synthesis of chlorinated acetylenes. For example, it is known, as shown above, that trichloroethylene,  $\text{CHCl}=\text{CCl}_2$ , in contact with hot alkali can be converted to  $\text{ClC}\equiv\text{CCl}$ , and that dry conditions favor this reaction. Since many of the pieces of equipment on board nuclear submarines can and indeed do act as chemical converters, it is important to know what the effect of each is in the transformation of halogenated hydrocarbons. The laboratory-scale  $\text{CO}/\text{H}_2$  burner has been modified and reactivated because it is known to cause the formation of corrosive acids and chlorinated organic compounds from the degradation of chlorinated hydrocarbons (14). The  $\text{Li}_2\text{CO}_3$  acid scrubber, the MEA carbon dioxide scrubber, and the high-pressure air compressors are other examples of equipment that need to be considered for possible synthesis of such compounds as the chlorinated acetylenes.

Work to date has shown that the chemistry of the decomposition of chlorinated hydrocarbons over Hopcalite catalyst containing lithium carbonate is complex. However, several generalizations can be made:

1. Methyl chloroform is almost completely destroyed at catalyst temperatures above 210°C (410°F). The principal intermediate degradation product is vinylidene chloride.
2. The yield of vinylidene chloride from methyl chloroform in the laboratory burner is considerably higher at 550°F than at 600°F.
3. Trichloroethylene is more stable under these conditions than is vinylidene chloride. When trichloroethylene is decomposed, the principal product is tetrachloroethylene. The mechanism of this reaction is not clear at this time.

#### WHAT TOXIC AGENT CAUSED THE TECUMSEH ILLNESSES DURING FIRST PATROL?

The incident of toxicity aboard USS TECUMSEH is unique in nuclear submarine history. Other nuclear submarines have had occasional atmospheric problems, such as difficulties with eye irritants (15,16), corrosive fumes (17), or localized odors, but none of these has ever given rise to such a widespread and incapacitating symptomatology as that experienced by TECUMSEH. As is often the case in tracing causative factors of toxicological effects, human subjects, in this case the crew of TECUMSEH, are usually the best indicators of the presence of a toxicant or irritant. To isolate and identify the toxicant from among the hundreds of chemical compounds aboard ship is a difficult task, particularly when the samples of atmosphere are known to be not truly representative of the occasion, as in this case. Although it is not possible at present to give the absolute identification of the toxic agent responsible for the TECUMSEH syndrome, a discussion of the various possibilities is presented.

Since the toxicity symptoms observed agree closely with those expected of many chlorinated hydrocarbons, the total atmospheric concentration of chlorinated compounds in the TECUMSEH atmosphere is of great interest. The fact that the combined organic desorbate from TECUMSEH carbon had a chlorine content of 19.6% by weight is impressive (see Table 5). This figure is compared in Table 8 with other data obtained in a similar way. Note particularly the data for sample C-392, from USS GRANT, which was obtained during its first patrol also. This sample should be particularly comparable since GRANT is a sister ship built at Electric Boat Co. during almost the same time period. The TECUMSEH sample, exposed for only one-third as long a time, contained the same amount of desorbed oil and more than six times as much chlorine as the GRANT sample. The CALHOUN sample, from its first patrol also, contained much less chlorine than the TECUMSEH sample, despite its longer exposure time and higher oil content.

Table 8  
Total Chlorine in Steam Desorbates from Main Filter Carbon

Sample No.	Ship	Patrol No.	Exposure (days)	Desorbed Oil (%)	Chlorine (wt-%)
C-389	TECUMSEH	One	12	6.8	19.6
C-392	GRANT	One	36	6.1	2.9
C-395	CALHOUN	One	44	14.5	2.9

Because of the relatively very high content of chlorinated hydrocarbons, the illnesses aboard TECUMSEH could possibly have resulted from a combined effect. In addition to the high total chlorine content, it should be noted that a total of fourteen halogenated hydrocarbons were identified in TECUMSEH samples (see Tables 2 and 6). The sources of a number of these compounds are discussed later. However, it can be stated in general that the halogenated compounds occur in nuclear submarine atmospheres in the following principal ways: as fluids in the ship's refrigeration plants, as solvents in materials of construction (17), as impurities in construction materials (18), and as degradation products of other compounds in shipboard apparatus such as the CO/H<sub>2</sub> burners (14). Solvents used during construction and refit periods are retained in insulation and coating materials and are contributed to the atmosphere during submergences.

It should be pointed out that halogenated compounds that are by themselves innocuous may be possible raw materials for synthesis of toxic compounds. Some of these possibilities will be explored in the following discussion, but the introduction of a pot-pourri of reactive chlorinated compounds into the CO/H<sub>2</sub> burner, for example, may lead to unexpected results when compared to reactions of individual compounds.

The discussion which follows includes consideration of a number of candidate toxic agents, with an estimate of the culpability of each. In view of the fact that toxic symptoms caused by many chlorinated hydrocarbons generally have a number of similarities to many of the symptoms reported by TECUMSEH, the chlorinated compounds are given special attention in the following discussion. Several other possible toxic agents are discussed also.

#### Dichloroacetylene

Consideration of all the factors in this case leads to dichloroacetylene,  $\text{CCl}\equiv\text{CCl}$ , as the most likely toxic atmospheric contaminant which may have caused the serious illnesses in the first patrol of TECUMSEH. Although this compound was present in the air sample at an estimated concentration of only 0.15 ppm, it is possible that the actual concentration in the ship's atmosphere was 1.0 ppm or higher. This follows from the dilution of the air sample in the air bank and the tenuous stability of the compound.

Although controlled toxicological studies of dichloroacetylene have not been made, this compound appears to be extremely toxic as shown by clinical evidence, primarily from British hospitals (19). A summary of the British medical experience is as follows. Trichloroethylene, being used as a general anesthetic, was in some instances passed through a carbon dioxide scrubber containing soda lime. Some of the trichloroethylene was converted by the alkali to dichloroacetylene. Several hours after exposures of one to a few hours, it was observed that the affected patients developed headaches and excessive vomiting, followed by anesthesia, paresthesia, and palsy in the trigeminal area. Facial herpes often resulted after a few days. The patients who died from exposures to dichloroacetylene displayed a syndrome of encephalitis which was confirmed by autopsy.

Although the concentrations of dichloroacetylene to which patients were exposed is unknown, the clinical observations indicate that this compound may be very toxic. Severe symptoms of cranial nerve involvement which resulted from the anesthesia applications as described above, for as little as 20 minutes, may have been caused by exposure to fairly low concentrations of this compound. Exposure of rats to dichloroacetylene prepared from trichloroethylene in air invariably caused death shortly after exposures of 30 minutes. Unfortunately the latter experiments also gave no clear statement of the concentrations involved.

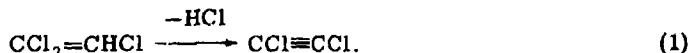
CONFIDENTIAL

Dichloroacetylene has been proved (20) to be the most probable toxic agent which caused the abort of a closed-atmosphere test being run by the Boeing Company for NASA. Project MESA, as it was known, was designed to test the effectiveness of a fully integrated, regenerative, life-support system in maintaining a habitable closed atmosphere for a five-man, thirty-day, simulated space flight (21). The study was being run in a 2350-cu ft steel vacuum chamber designed by the Boeing Company.

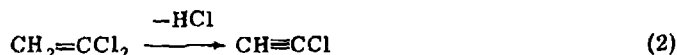
Because of a number of alarming symptoms which developed in the men, it became necessary to abort the MESA test after 4-1/2 days. The entire five-man crew suffered the same symptoms: an initial feeling of general malaise, followed by loss of appetite and nausea of increasing frequency. Other symptoms were headaches, eye irritation, soreness of gums and jaws with slight bleeding in some cases. The perspiration and urine of one crew member, for a number of hours after the abort, emitted a sweet-sour, pungent odor identical to the one which permeated the chamber. The crew was also afflicted shortly after the abort with large welts or cold sores around the mouth. Analyses of samples of atmosphere taken on adsorbents following this incident yielded a number of contaminants, including trichloroethylene, dichloroacetylene, and chloroacetylene. The involvement of parts of the life-support system in generation of the chlorinated acetylenes seems very likely. The Hopcalite burner was being operated at a temperature much lower than the 600°F specified for submarines. It is also possible that other units — a sodium superoxide unit, activated carbon, silica gel, and a sewage and waste water processing plant — were involved.

The symptoms in Project MESA were remarkably similar to those reported in the British medical cases of dichloroacetylene intoxication. Even the very unusual facial herpes (cold sores) were also observed in the MESA crew. Although the symptoms in the TECUMSEH crew were somewhat different from the MESA ones (for example, no herpes were in the TECUMSEH crew, and no constipation or chest muscle soreness with the MESA crew), the similarities of the reported instances point up the strong possibility of a similar causative agent.

It is quite possible that the operation of the CO/H<sub>2</sub> burner at 550°F in TECUMSEH in an atmosphere containing high concentrations of a number of chlorinated hydrocarbons was a strong contributing factor. It is known from studies at NRL (14), for example, that methyl chloroform decomposes to yield vinylidene chloride at 600°F, with higher yields at lower temperatures. Trichloroethylene is also a product of methyl chloroform decomposition, although at a much lower yield. From whatever source it arose, the lower burner temperature would favor buildup of trichloroethylene. Trichloroethylene in passing over alkali under certain conditions is known to produce dichloroacetylene, CCl<sub>2</sub>=CCl. A simplified illustration of this reaction is given by



The equation



similarly depicts the possible production of monochloroacetylene (CH=CCl) from vinylidene chloride. Very little is known about the preparation and toxicity of CH=CCl, and further work is needed in this regard. Nevertheless, it is suggested that both of the chlorinated acetylenes may result from the reaction of the parent compounds in alkaline media, such as LiOH pellets or monoethanolamine (MEA) solution. A more detailed

discussion of the intricacies of the decomposition of the various chlorinated hydrocarbons in the CO/H<sub>2</sub> burners and other shipboard equipment must await the outcome of laboratory studies now underway.

It may be recalled that a "sweet, unpleasant, sour odor" was noted by TECUMSEH personnel. This description is very similar to the "sweet-sour, pungent odor" reported by MESA personnel. In this regard, it can be stated also that the odor of the NRL preparation of dichloroacetylene had similar characteristics and matched very closely a distinctive odor present in the main filter carbon (C-589) from TECUMSEH.

#### Vinylidene Chloride

Of all the chlorinated compounds listed in Table 2 and Table 6, other than dichloroacetylene, the one with the highest probability of toxic involvement seems to be vinylidene chloride, CH<sub>2</sub>=CCl<sub>2</sub>, both because of its high concentration, which may have been as much as 5 to 10 ppm, and its high order of toxicity. Although toxicology studies are not complete, a maximum allowable concentration (MAC) of 5 ppm has been set as a submarine guideline for continuous 60 to 90 day exposures (22). One of the factors which obviously would have been conducive to a high atmospheric concentration of vinylidene chloride was the lower operating temperature of the CO/H<sub>2</sub> burners for a number of days just prior to the development of toxic symptoms. This lower temperature would lead to a higher yield of vinylidene chloride from methyl chloroform and a lower rate of destruction of vinylidene chloride, as has been shown by recent NRL studies.

It should also be pointed out that vinylidene chloride is a likely precursor to a possibly very toxic compound, monochloroacetylene, CH≡CCl, of which very little is known.

#### Methyl Chloroform

The direct toxic effect of methyl chloroform, CH<sub>3</sub>CCl<sub>3</sub>, was probably very little. A number of other instances of high concentration of this compound in FBM submarines have not led to noticeable toxicological effects. The involvement of methyl chloroform may have been considerable, however, in its conversion to vinylidene chloride in the CO/H<sub>2</sub> burner (14). Methyl chloroform can yield also trichloroethylene, and perhaps its daughter product dichloroacetylene, in the CO/H<sub>2</sub> burner, although present knowledge indicates this process is probably not the primary source of these two compounds. Methyl chloroform itself undoubtedly occurred in the TECUMSEH atmosphere as a result of its use as a solvent in contact cement for application of hull insulation and other materials of construction (17). This solvent will continue to be supplied to the atmosphere by this source for a considerable time.

#### Trichloroethylene

Trichloroethylene has been discussed in detail earlier as the probable source of a major toxic suspect, dichloroacetylene. Trichloroethylene would not seem to have any direct toxic effect, except as a possible additive effect in the combined stress of chlorinated hydrocarbons. Although it has been demonstrated in recent work at NRL that modest yields of trichloroethylene can result from decomposition of methyl chloroform, it seems unlikely in view of present data that the amounts found in TECUMSEH samples could have resulted from conversion in the CO/H<sub>2</sub> burners. Operation of the burners at lower than

CONFIDENTIAL

600°F, however, would favor higher yields of trichloroethylene and its accumulation in the atmosphere.

Another possible source of trichloroethylene is its presence as a contaminant in other solvents. For example, it has been found in one common source of technical-grade methyl chloroform at more than 7% by volume (18). In addition, trichloroethylene may have occurred as a result of substantial use of this solvent in pre-patrol work, since it is a commonly used cleaning and degreasing solvent. Solvents used during periods of ventilation can by various means remain in paints, polymers, and other materials of construction, to be contributed to the submarine atmosphere during submergences.

#### Tetrachloroethylene

Although discovered to be a large component of the chlorinated hydrocarbon content of the TECUMSEH samples, tetrachloroethylene is ruled out as a primary toxicant because of its relatively high threshold limit value (TLV). It is not known at present if this compound,  $\text{CCl}_2=\text{CCl}_2$ , yields toxic organic decomposition products in the  $\text{CO}/\text{H}_2$  burner or other equipment. However, this possibility is presently under study. It would appear that tetrachloroethylene was present in TECUMSEH atmosphere as a direct result of its use as a solvent or a solvent composition, possibly in pre-patrol work.

#### Freon-Type Compounds

Five compounds of this type, fluorochloro or fluorobromo compounds, were found in various amounts as shown in Table 9. None of these compounds is known to be toxic at the concentrations listed. Furthermore, there is no information at present which suggests that decomposition products of these compounds may have caused the toxic symptoms. Freon-11, Freon-12, and Freon-114B2 are used on board ship as refrigerants. Freon-113 and Freon-114 are finding increasing use in industry as cleaning solvents and may have occurred aboard ship in this way. It is known that some Freon-113 was so used. The possible chemical conversion of some of these compounds to toxic compounds needs to be studied.

Table 9  
Freon-Type Compounds Found in  
TECUMSEH Atmosphere Samples

Compound	Formula	Concentration Found* (ppm)
F-12	$\text{CCl}_2\text{F}_2$	52
F-11	$\text{CCl}_3\text{F}$	4.0
F-114	$\text{CClF}_2-\text{CClF}_2$	1.5
F-113	$\text{CCl}_2\text{F}-\text{CClF}_2$	0.6
F-114B2	$\text{CBrF}_2-\text{CBrF}_2$	trace

\*Actual concentrations may well have been 2 to 3 times higher.

#### Various Chlorinated Hydrocarbons

Traces of chloroform, carbon tetrachloride, and two chlorofluoroethanes were found. These do not appear to be directly implicated. However, it should be stated once more that the combined effect of a number of halogenated atmospheric contaminants should not be ignored.

#### Lithium Carbonate Dust

As was stated earlier, what appeared to be an inordinate amount of white dust was deposited in certain areas of the ship. This dust was characterized by the ship's crew as certainly being  $\text{Li}_2\text{CO}_3$  from the acid scrubber for the  $\text{CO}/\text{H}_2$  burner effluents. Although curiously enough some lithium salts can cause poisoning with symptoms similar to those observed, this dust, although objectionable, is most probably not the toxic agent in this case. The fact that the dust was not distributed throughout the ship, as the illnesses actually were, seems to rule out  $\text{Li}_2\text{CO}_3$ . Nevertheless, serum and urine specimens were taken by the U.S. Navy Preventive Medicine Unit No. 6 a few weeks after the end of the patrol and analyzed at the Sixth U.S. Army Medical Laboratory, Fort Baker, California. The results of the analyses were interpreted to indicate very slight if any lithium salt involvement in this case (23).

#### Phosphine

As much as 16 cu ft (STP) of acetylene may have leaked into the submarine atmosphere from a cylinder aboard TECUMSEH. The rate of leakage is not known but could have extended over a period of 30 days.

Phosphine ( $\text{PH}_3$ ) is a gaseous impurity normally present in small quantity in acetylene produced from calcium carbide, and would, if present, have passed into the submarine atmosphere along with the acetylene. The present industrial TLV for phosphine is 0.3 ppm, and a submarine guideline, although not established, would undoubtedly be lower, possibly 0.1 ppm (24). However, the toxic symptoms seem not to fit very well those described for TECUMSEH. Its toxic properties are described in Ref. 25. As the worst case, if the acetylene cylinder contained the maximum permissible content of 0.05% of phosphine (26), it was calculated that sudden admittance of the entire 40 cu ft of lost acetylene all at once into a 170,000-cu ft space would produce a transient, localized toxic and combustible hazard. As soon as uniformly mixed in the space, the acetylene concentration would be 1% of the lower explosive limit and the phosphine concentration would be 0.12 ppm. Such an exposure to phosphine is unlikely to have caused the TECUMSEH toxicity. Furthermore, passage through the  $\text{CO}/\text{H}_2$  burner should begin immediately to decrease even this low concentration.

Examination of the TECUMSEH air bank sample indicated that the phosphine concentration, if any, was less than 0.03 ppm, which is less than one-tenth of the current TLV value and about 1/3 of the estimated submarine guideline value.

The conclusion seems fairly definite that phosphine was not the toxic agent in the TECUMSEH case.

The possible contribution of acetylene,  $\text{CH}\equiv\text{CH}$ , to synthesis of dichloroacetylene in the submarine is unknown but seems much less likely than formation by degradation of trichloroethylene.

### Other Candidate Toxic Agents

A large number of other possible toxic agents were considered in searching for the explanation to the TECUMSEH problem. A number of them were ruled out because of the poor match with the observed symptoms. Others were eliminated because of their absence in the atmosphere of TECUMSEH in toxic concentrations. For example, nitrous oxides and phosgene were not detected with the detector tubes used by the crew. This, together with the lack of irritating symptoms, eliminated these agents from further consideration. This illustration emphasizes the value of testing the atmosphere with the complete set of detector tubes available whenever a toxic atmospheric contaminant is suspected.

### CONSEQUENCES OF THE TECUMSEH INCIDENT

The very serious implications of the occurrence of widespread illnesses during the first patrol of TECUMSEH prompted a number of actions and reactions. This event brought home to many people the fact that atmospheric contamination in nuclear submarines can cause serious physiological problems. It is evident that too many unknowns exist in our knowledge of atmosphere control in this sense. The following items summarize the actions taken thus far:

1. Almost immediately it was suspected that operation of the CO/H<sub>2</sub> burners at temperatures below 600°F may have been a major contributing factor to the problem. Therefore, it was recommended that, during the second patrol of TECUMSEH, the burners be operated at 600°F, and no lower (7). In addition, it was recommended that the Squadron Fifteen policy that main filter carbon be changed every 20 days be strictly followed. Other recommendations concerned containment of Li<sub>2</sub>CO<sub>3</sub> fines, electrostatic precipitator operation, and absolute control of chlorinated solvents.

2. A special sampling program was initiated with Squadron Fifteen. Main filter carbon samples and compressed atmosphere samples have been taken on a regular schedule. The latter were obtained using a small oil-free compressor and stainless steel sample bottles supplied by NRL. This program had a twofold purpose: to provide background information on atmospheres in a series of new FBM submarines during patrol operations, and to assist in formulating a special sampling kit and instructions for use in an emergency such as in TECUMSEH.

3. A breath-sampling study was made on a portion of the personnel of TECUMSEH (Gold) at the end of the second patrol. This study was made with the cooperation of Lt Cdr H. E. Glick (MC) USN, Squadron Medical Officer, SubRon Fifteen, and Dr. R. D. Stewart of the Dow Chemical Company. The aim of the study was to determine whether it was feasible to detect chlorinated hydrocarbons in breath samples from men exposed to these compounds during a submergence. Trace amounts of methyl chloroform, for example, were found in the breath samples from all the crew sampled (27). It was demonstrated that such a procedure is entirely feasible. However, it is suggested that the Bureau of Medicine and Surgery should determine the value of setting up a further program along these lines.

4. A number of laboratory studies were initiated. A study of the decomposition and conversion of various halogenated compounds in a bench-scale CO/H<sub>2</sub> burner was reactivated. In addition, the stability of these compounds under other conditions existing aboard submarines will be studied. Studies have begun on preparation and properties of such unusually toxic compounds as dichloroacetylene.

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5. The Navy Toxicology Unit under Capt J. Siegel is studying the toxicology of a number of chlorinated compounds: trichloroethylene, methyl chloroform, vinylidene chloride, carbon tetrachloride, and dichloroacetylene. Special attention is being given to toxicity studies of dichloroacetylene, which poses special difficulties because of the instability of this compound under most conditions.

#### CONCLUSIONS

It is concluded that dichloroacetylene,  $\text{ClC}=\text{CCl}$ , is the most likely atmospheric contaminant to have caused the widespread illnesses of the crew during the first patrol of USS TECUMSEH. Although the toxicity of dichloroacetylene has not been established quantitatively, it is undoubtedly of a high order. This compound, which was found in a TECUMSEH air sample, probably resulted from the decomposition of trichloroethylene in the  $\text{CO}/\text{H}_2$  burners. The trichloroethylene itself is a known decomposition product of methyl chloroform and vinylidene chloride, although other sources may have contributed to its vapor concentration in the submarine. The operation of the  $\text{CO}/\text{H}_2$  burners at  $550^\circ\text{F}$  for an extended period was undoubtedly a contributing factor, because the lower temperature favors formation and buildup of these chlorinated decomposition products.

In an atmosphere characterized by a high total content of chlorinated hydrocarbons, another strong suspect is vinylidene chloride,  $\text{CH}_2=\text{CCl}_2$ . This compound is a decomposition product of methyl chloroform which has appeared in large quantities in recent nuclear submarines because of its use in adhesives for construction purposes. Other possible toxic agents were discussed earlier.

It is concluded further that the continued use of chlorinated solvents in nuclear submarines may, at a future time, due to certain combinations of circumstances, again cause serious toxicological effects on the crew. Although USS TECUMSEH has had two subsequent patrols without such difficulty, the incomplete understanding of the cause of the events of the first patrol make it impossible to ensure prevention of a similar incident, perhaps in another submarine. Elimination of chlorinated compounds in nuclear submarines should be an immediate goal.

#### RECOMMENDATIONS

1. It is recommended that the use of chlorinated solvents in nuclear submarines be eliminated as much as possible at all times. These solvents should be absolutely forbidden during submergences. It has been found, in this regard, that such use during out-board ventilation can still contribute chlorinated hydrocarbons to the atmosphere during subsequent submergences, by sorption and later desorption from the multiplicity of materials in the space.

2. It is recommended specifically that the use of trichloroethylene be absolutely forbidden in nuclear submarines at all times. This compound is very hazardous because of the possibility of its conversion under certain conditions to dichloroacetylene, which may be very toxic.

3. It is recommended that the use of chlorinated solvents in materials of construction be eliminated.

4. It is recommended that the  $\text{CO}/\text{H}_2$  burners not be operated below  $600^\circ\text{F}$ . Present knowledge indicates that lower temperatures favor the synthesis of toxic chlorinated compounds.

CONFIDENTIAL

5. It is recommended that all main filter carbon beds be changed every 20 days during submergences, especially during the first year of operation.

6. It is recommended that the personnel of nuclear submarines be instructed to report promptly the presence of any abnormal odor, respiratory irritation, or other physiological response which might be indicative of submarine atmosphere contamination, so that suitable action may be taken.

7. It is recommended that nuclear submarines should carry out routine, periodic atmosphere surveys using all available colorimetric gas detector tubes and other means of detection of contamination. Positive indication, though small, should be considered significant and inspire action to locate and remove the source of the contaminant and other appropriate action. Such data will be helpful should any future toxic contamination occur.

8. It is recommended that the Bureau of Medicine and Surgery consider the advisability of exploring further the sampling of breath from FBM crews, particularly in those men exposed to chlorinated hydrocarbons.

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CONFIDENTIAL

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<p>A high percentage of the personnel of USS TECUMSEH (Blue) became ill after about 30 days' submergence during the ship's first patrol. In many cases symptoms were quite severe. The characteristics of the illnesses strongly implicated a toxic agent rather than infection as the cause. Study of atmosphere samples and related information indicated that the illness was related to the high content of chlorinated hydrocarbons in the atmosphere. Although the specific toxicant has not been identified, two of the most likely suspects are dichloroacetylene and vinylidene chloride. There is also the possibility of the combined effect of a number of halogenated compounds. Elimination of chlorinated compounds in nuclear submarines should be an immediate goal.</p>		

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14. KEY WORDS	LINK A		LINK B		LINK C	
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